

far as the concentration in the effective layer from which the absorption lines originate is concerned. The problem, however, awaits further investigation.

In spite of the uncertainty in choosing the proper concentration for a given element, it will be admitted from what has gone before that the temperature plays the leading rôle in determining the nature of the stellar spectrum. Too much importance must not be attached to the figures given, for the theory is only a first attempt for quantitatively estimating the physical processes taking place at high temperature. We have practically no laboratory data to guide us, but the stellar spectra may be regarded as unfolding to us, in an unbroken sequence, the physical processes succeeding each other as the temperature is continually varied from 3000° K. to 40,000° K.

In conclusion, it is my great pleasure to record my best thanks to Prof. A. Fowler for the interest he has taken in the work, and the many valuable items of information, advice, and criticism with which he has helped me. I also wish to express my thanks to Mr. S. K. Ghosh, M.Sc., of the Calcutta University, for much useful help in the preparation of this paper.

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*On the Catalytic Dehydrogenation of Alcohols.*

By ERIC KEIGHTLEY RIDEAL.

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In spite of the numerous industrial processes developed for the hydrogenation of various organic substances with the aid of catalytic materials, but little work has been accomplished on the determination of the mass action equilibrium constants of organic substances which undergo thermal dissociation. Thus in the dissociation of ethyl alcohol into acetaldehyde and hydrogen, or of isopropyl alcohol into acetone and hydrogen, two reactions widely employed, the dependence of the degree of the dissociation on the temperature is unknown. Sabatier ('*La Catalyse en Chimie Organique*') states (p. 82) that acetaldehyde is easily hydrogenated at 140° C. and acetone at a temperature of 115° to 125° C. utilising nickel as a catalytic agent.

At higher temperatures, however, 200° to 350° C., acetone is not hydrogenated to isopropyl alcohol, but methyl isobutylketone and diisobutylketone are

produced. Again (p. 161) ethyl alcohol undergoes rapid dehydrogenation at a copper surface within the temperature range  $200^{\circ}$  to  $350^{\circ}$  C.; at  $420^{\circ}$  C. the acetaldehyde produced undergoes decomposition. Isopropyl alcohol in contact with the same catalytic agent slowly commences to undergo dehydrogenation at  $150^{\circ}$  C., dehydrogenation being rapid at  $250^{\circ}$  to  $430^{\circ}$  C.

It is evident that these reactions are reversible and that the mass action equilibrium constants should be capable of experimental determination if the main reactions proceed smoothly without side reactions occurring to any appreciable extent. According to Sabatier the temperature range suitable for experimental investigation for both these alcohols lies within the range  $100^{\circ}$  to  $350^{\circ}$  C.

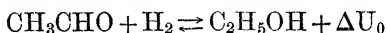
That nearly complete hydrogenation or dehydrogenation can be effected within such a small temperature range, is confirmed by application of the Nernst heat theorem, utilising the approximation formula. A closer estimation of the dissociation constants of the alcohols by this method is at present impossible, owing to our lack of knowledge of the heats of reaction and the specific heat data.

The approximation formula however indicates clearly that large changes in the values of the dissociation constants are to be expected within a very narrow range of temperature variation and at comparatively low temperatures.

The following values are found in the literature (Landolt Börnstein Tabellen) for the heats of combustion of the various constituents at constant pressure. Owing to lack of information as to the variation of the specific heats with the temperature the values of  $\Delta U_{18^{\circ}\text{C.}}$  will be taken as equal to  $\Delta U_{0^{\circ}\text{K.}}$

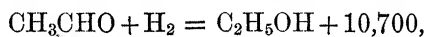
	Kgm. cal.
$\text{H}_2$ .....	58.1
$\text{CH}_3\text{CHO}$ .....	275.5-281.1
$\text{CH}_3\text{COCH}_3$ .....	427.2-437.3
$\text{C}_2\text{H}_5\text{OH}$ .....	326.1-340.5
Isopropyl alcohol .....	478.7-493.3

The values of the heat of reaction may accordingly vary within wide ranges, thus the value of  $\Delta U_0$  for the reaction



may vary from +13,900 calories to -6,900 calories according as the upper or lower values for the heat of combustion are taken; the two positive values are 13,900 and 7,500 giving a mean value of 10,700 calories, which will be the one adopted. In the case of the dissociation of isopropyl alcohol there is a similar variation from 16,700 calories to -7,900 calories. The two positive

values being 16,700 and 6,700 with a mean of 11,800 calories. On application of the approximation formula of the Nernst heat theorem to the reaction :



$$K_p = \frac{P_{\text{H}_2} \cdot P_{\text{CH}_3\text{CHO}}}{P_{\text{C}_2\text{H}_5\text{OH}}},$$

$$\log_{10} K_p = -\frac{\Delta U_0}{4.571T} + 1.75 \sum \nu \log_{10} T - \frac{\beta T}{4.571} + \sum \nu C_0.$$

Taking the chemical constants of the alcohol and aldehyde as equal to one another, the chemical constant of hydrogen as 2.2, and the variation of the specific heats of the reacting organic substances as compensating one another we obtain

$$\log_{10} K_p = -\frac{10,700}{4.571T} + 1.75 \log_{10} T - 3.75 \cdot 10^{-4} T + 2.2,$$

where  $\beta$  is the variation of the specific heat of hydrogen with the temperature.

Evaluating this expression we obtain

T.° K.	$\log_{10} K_p$ .
200	-5.55
300	-1.38
400	+0.63
500	+2.05

Similarly with the reaction



Making the same assumptions with respect to the temperature variation of the specific heats and the chemical constants of the ketone and the alcohol we obtain :

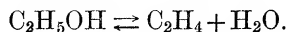
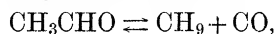
T.° K.	$\log_{10} K_p$ .
200	-6.75
300	-2.17
400	+0.03
600	+1.78

It is evident, from Sabatier's data, that the values of  $K$ , as determined by the Nernst approximation formula, are somewhat too high, although the extremely rapid variation of the constant with the temperature is clearly evident. The variations of the specific heats of the alcohols aldehyde and ketone with the temperature are probably extremely great, since such substances, capable of possessing many degrees of freedom, have, as a rule,

a high temperature coefficient for the specific heat, as can be instanced in the case of ether, which has the following values :—

$C_p$ .	Temperature °C.
32	0
32.6	100
41.6	200

Preliminary experiments indicated that the dynamic or flow method of determining the equilibrium was unsuitable, owing to the fact that at low temperatures, even with a very considerable length of catalytic material in a column, unchanged alcohol in large excess was invariably present in the effluent gases. The static method is less objectionable, although side reactions occur, all the more important when the reactants are exposed to the catalytic material for prolonged periods of time. The catalytic activity of various substances for these reactions varies extensively. Thus, with platinum black, and to a less extent with reduced nickel, both the aldehyde and the alcohol undergo partial decomposition relatively quickly :—



The carbon monoxide and ethylene thus produced may undergo still further reactions by hydrogenation, the former to methane and the latter to ethane.

The behaviour of acetone at high temperatures has already been noted ; even at low temperatures, acetaldehyde is unstable, undergoing both polymerisation and aldol condensation, with loss of water.

Metallic copper was found to be the most suitable catalytic agent to employ, since its catalytic activity for the reaction of hydrogenation and dehydrogenation is quite marked, whilst disturbing secondary reactions take place relatively slowly on its surface.

It was also found necessary to work with relatively low partial pressures, a closer approximation to the conditions of reversibility being obtained, doubtless associated with the stability of the aldehyde under these conditions.

Although the dissociation of the alcohol to aldehyde and hydrogen takes place relatively rapidly at the commencement, yet the reverse reaction proceeds but slowly, and a long period of contact is necessary even to approximate to equilibrium conditions. According to the general concept of catalytic mechanism, an alcohol molecule striking the surface of the catalyst may either undergo decomposition or it may evaporate from the surface unchanged. For the combination of aldehyde and hydrogen, a molecule of each species has to strike adjacent molecules of the catalytic surface : a much less frequent phenomenon. The following calculation

indicates that, unless the number of alcohol molecules striking the surface and evaporating again unchanged is extraordinarily large, the reverse reaction will proceed much more slowly.

If pure alcohol vapour be brought into contact with the catalytic surface, the number of gramme-molecules of alcohol striking each square centimetre of surface per second will be

$$\frac{43.75 \cdot 10^{-6}}{\sqrt{(MT)}} \cdot p,$$

where  $M$  is the molecular weight of the alcohol,  $T$  the temperature in degrees K, and  $p$  the pressure in bars.

If, on the other hand, an aldehyde hydrogen mixture be brought into contact with the catalyst, and we assume that an aldehyde molecule occupies a position,  $X$ , on the molecular lattice of the catalyst, the chance

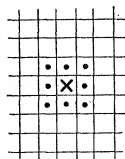


FIG. 1.

of combination is dependent on the probability that a molecule of hydrogen will occupy one of the surrounding eight squares. If  $p'$  be the partial pressure of the hydrogen of molecular weight  $M_0$ ,  $\sigma$  the life of a hydrogen molecule on the surface, and  $d$  the molecular diameter; then the fraction of the unit area covered with hydrogen will be

$$\frac{43.75 \cdot 10^{-6}}{\sqrt{(M_0 T)}} \cdot p' \cdot \sigma \pi d^2,$$

the probability that a molecule of aldehyde will be in contact with one of the hydrogen will be

$$8 \left( \frac{43.75 \cdot 10^{-6}}{\sqrt{(M_0 T)}} \right) p' \cdot \sigma \cdot \pi d^2.$$

This is equal to the total number of contacts divided by the total number of molecules of aldehyde on the surface.

If  $x$  be the total number of contacts,  $p'$  the partial pressure of the aldehyde, in this case equal to that of the hydrogen,  $\sigma'$  the life of an aldehyde molecule on the surface,  $M_1$  its molecular weight, then

$$\frac{x}{\frac{43.75 \cdot 10^{-6}}{\sqrt{(M_1 T)}} \cdot p' \sigma'} = 8 \left( \frac{43.75 \cdot 10^{-6}}{\sqrt{(M_0 T)}} \right) p' \pi d^2 \sigma,$$

therefore 
$$x = 8 \left( \frac{43.75 \cdot 10^{-6}}{\sqrt{(T)}} \right)^2 \cdot \frac{1}{\sqrt{(M_0 M')}} \cdot p'^2 \cdot \pi d^2 \cdot \sigma \sigma'.$$

Whilst for the unimolecular alcohol decomposition the rate of reaction was found to be

$$\frac{43.75 \cdot 10^{-6}}{\sqrt{(MT)}} \cdot pX,$$

where  $X$  is the fraction of the molecules striking which undergo decomposition.

The ratio of the two velocities is accordingly given by

$$\begin{aligned} \frac{\text{v. hydrogenation}}{\text{v. dehydrogenation}} &= \frac{8 \left( \frac{43.75 \cdot 10^{-6}}{\sqrt{(T)}} \right)^2 \frac{1}{\sqrt{(M_0 M_1)}} \cdot p'^2 \pi d^2 \sigma \sigma'}{\frac{43.75 \cdot 10^{-6}}{\sqrt{(MT)}} p \cdot X} \\ &= \frac{3.5 \cdot 10^{-4} \cdot p_1^2 \pi d^2 \sigma' \sigma \sqrt{(M)}}{\sqrt{(M_0 M_1 T)} \cdot p \cdot X}. \end{aligned}$$

According to Langmuir\* the average life of a molecule on the surface of a solid is given by the expression

$$\sigma = 22860 a \sqrt{(MT)},$$

where  $a$  is determined approximately from the empiric Freundlich isotherm

$$q = ap^{1/n}.$$

If a value of  $5 \cdot 10^{-8}$  cm. is adopted for  $d$ , the molecular diameter,  $T$  as  $500^\circ \text{K.}$ ,  $p' = 0.5$  megabar, and  $p = 1.0$  megabar, the ratio of the two velocities will be

$$\frac{\text{v. hydrogenation}}{\text{v. dehydrogenation}} = \frac{358.6 \cdot 10^{-6} a_1 a_2 \sqrt{(MT)}}{X} = \frac{5.45 \cdot 10^{-2} a_1 a_2}{X}.$$

The values of  $a_1$  and  $a_2$  for hydrogen and acetaldehyde respectively at this temperature are probably very small and that for hydrogen considerably less than that for the aldehyde. If arbitrary values of  $a_1 = 0.01$  and  $a_2 = 0.1$  are adopted, the velocity of decomposition will be no less than 20,000 times the velocity of hydrogenation if the value of  $X = 1$ . Elevation of both temperature and pressure reduces the disparity between the two reaction rates.

The general mode of procedure accordingly was to determine the dissociation of the alcohol in contact with metallic copper under reduced pressures, the constant volume method being adopted. When dissociation was nearly complete, the temperature was allowed to fall and the degree of combination ascertained. Under conditions of true reversibility the two curves plotted from the results should naturally coincide. It was found in general that slight decomposition could not be avoided, and that, although the decomposition curves could be repeated, the values obtained for the process of hydro-

\* 'J. Amer. Chem. Soc.,' vol. 40, p. 1390 (1918).

generation were by no means so regular. If sufficient time were given for the system to arrive at equilibrium, secondary decomposition occurred relatively rapidly at high temperatures, and after two or three hours' contact at low temperatures.

*Experimental.*

Short pieces of copper wire were repeatedly oxidised and reduced, first in hydrogen and subsequently in ethyl alcohol vapour at continually decreasing temperatures until the surface of the metal underwent spontaneous oxidation on exposure to air at room temperature, the final reduction being performed when the catalyst was in place in the apparatus. The apparatus consisted of a simple constant-volume gas thermometer, the bulb being a piece of glass tube, 15 cm. long and 1.5 cm. diameter, containing 5 gm. of the reduced catalytic copper. The bulb was connected by means of a piece of thick-walled tube to a mercury manometer, provision being made by means of a T-piece and two-way tap, for the evacuation of the bulb and for the admission of the alcohol.

The reaction vessel was heated in an electric furnace, sufficiently long as to ensure the uniformity of temperature over the whole length of the tube.

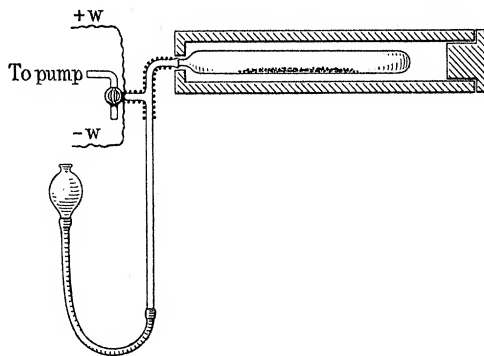


FIG. 2.

To prevent condensation occurring in the system on the top of the mercury in the manometer, the exposed portion of the thin tube was wound with nichrome wire and covered with asbestos, the temperature being maintained, by means of an electric current, at 100° C. during the period of each experiment.

For each experiment the system was evacuated by means of a Sprengel mercury pump, a small quantity of alcohol admitted, and the catalyst freshly reduced at a temperature of 250° C. The tube was then re-evacuated and the temperature maintained at 275° C. to ensure removal of absorbed and dissolved gases.

After cooling a small quantity of the alcohol was admitted and the temperature pressure curve determined at constant volume, time being given for the system to come to equilibrium. Four to five hours were found necessary at the lower temperatures and half an hour at the higher.

The temperature pressure curve was likewise determined during the process of cooling. Long periods of time were generally necessary for the pressure to attain a constant value and it was generally observed that slight secondary decomposition was unavoidable.

Both the ethyl and isopropyl alcohols were pure and free from water.\*

As typical of the variations of pressure with the temperature the following table may be cited.

Temperature °C.	Ethyl alcohol.		Isobutyl alcohol.	
	Pressure in mm. Hg.		Pressure in mm. Hg.	
	Heating.	Cooling.	Heating.	Cooling.
20	36	—	18	—
50	64	—	42	—
75	74	75	60	74
100	81.5	83	100	105
125	93	94	119	120
150	102	106.3	145	158
175	114	125	180	204
200	128	148	218	240
225	149	177	250	262
250	185	220	272	277
275	242	261	289	289
300	335	335	—	—

It will be noted that a secondary irreversible decomposition had taken place to a limited extent with each alcohol, since the pressures on the cooling curve are uniformly higher than those on the heating curve. From these data the percentage decomposition at the respective partial pressures was determined, it being assumed that complete vaporisation of the alcohol was effected at 100° C., and at this temperature and pressure the simple gas laws were valid.

If  $x$  be the degree of dissociation at any definite temperature and at a pressure of  $p$  mm. of mercury the dissociation constant for one atmosphere is obtained from the expression

$$K_p = \frac{x^2}{1-x} \frac{p}{760}.$$

In the following table are given the values of  $K_p$  determined from the mean of three experiments on each alcohol, the heating curve alone being

\* I am indebted to Mrs. W. G. Palmer for having kindly provided me with carefully purified specimens of these materials.



utilised for the purpose of calculation. Appended also are given the percentage decompositions of each alcohol under a total pressure of one atmosphere

Temperature °C.	Ethyl alcohol.		Isopropyl alcohol.	
	$K_p$ .	Per cent. decomposition at 1 atmosphere.	$K_p$ .	Per cent. decomposition at 1 atmosphere.
105	$6.44 \cdot 10^{-4}$	2.5	$2.82 \cdot 10^{-3}$	5.3
150	$1.60 \cdot 10^{-3}$	3.9	$2.04 \cdot 10^{-2}$	13.6
175	$4.77 \cdot 10^{-3}$	6.7	0.177	29.0
200	$1.21 \cdot 10^{-2}$	10.6	0.523	51.1
225	$4.52 \cdot 10^{-2}$	19.5	1.35	66.9
250	$2.32 \cdot 10^{-1}$	38.0	4.82	85.0
275	0.91	60.2	12.0	92.8

If the values of  $\Delta U_0$  be calculated for each 25° C. rise by means of the Van t'Hoff equation, the heat of reaction for the dissociation of ethyl alcohol is found to rise from 12,100 calories at 125° C. to 30,500 calories per gramme-molecule at 275° C., whilst for the same temperature range the values for the dissociation of isopropyl alcohol are 25,200 and 20,000 calories per gramme-molecule respectively: this latter substance yielding a mean value of 21,300 calories per gramme-molecule.

In the case of ethyl alcohol the high values obtained are probably due to secondary decomposition of the aldehyde, which is much less stable than acetone.

The value of  $\Delta U_0$  obtained from the value of  $\Delta U_{373} = 12,100$  and from the specific heats of the reactants and products.

$$\frac{d\Delta U}{dT} = C_1 - C_2 = 15.80 + 6.82 - 20.84 = 1.78,$$

is 11,500 calories per gramme molecule for ethyl alcohol.

For isopropyl alcohol, taking the specific heat of isopropyl as 27.80 we obtain

$$\frac{d\Delta U}{dT} = 23.95 + 6.82 - 27.80 = 2.97,$$

and  $\Delta U_{373} = 21,300$  or  $\Delta U_0 = 20,100$ .

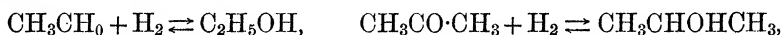
The mean value of  $\Delta U_0$  determined from the heat of combustion of ethyl alcohol was 10,700 calories and from the dissociation curve 11,500 calories. If this figure were corrected for the effect of the alteration of the specific heats with the temperature, on which data are not available, still closer agreement might be obtained.

In the case of isopropyl alcohol there is a very large discrepancy between the mean value of 21,300 calories obtained from the dissociation curve and the mean value of 11,800 calories obtained from data on the combustion of isopropyl alcohol and acetone. The maximum value of 16,700 calories per gramme-molecule is even exceeded.

The heats of combustion of these substances are, however, so large that an error of less than 1 per cent. in the determination would more than compensate for the observed difference. A variation of nearly 3 per cent. in these determinations is actually recorded.

*Summary.*

In confirmation of Sabatier's experiments the application of the Nernst approximation formula indicates that the variation of the dissociation constants of the equilibria



with the temperature are extremely large. The velocity of decomposition at the surface of a solid catalyst is shown to be very much higher than the reverse reaction of hydrogenation. The variation of the values of the dissociation constants with the temperature was experimentally determined with a constant volume thermometer containing carefully reduced copper as catalytic material. Concordant values could not be obtained at atmospheric pressures, but a closer approximation to reversibility was obtained when low pressures were employed. The value of  $\Delta U_0$  for the decomposition of ethyl alcohol was found to be 11,500 calories, whilst the mean value determined from the heats of combustion is 10,700. In the case of isopropyl alcohol the respective values for  $\Delta U_0$  are 21,300 and 11,800. In the latter case an error of less than 1 per cent. in the determination of the heat of combustion of the alcohol would account for the discrepancy.

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